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Elastic Scattering of Low-Energy Electrons at 180° in CO_2†

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A technique is described for the study of electrons which are elastically scattered from a gas target into a small solid angle centered at 180° with respect to the direction of the incident electron beam. The method is applied to electron scattering from CO_2. Information is obtained concerning the nature of the compound state in the 4-eV region.

Measurement of the elastic scattering of electrons from molecules at 180° offers a number of advantages for the detection of the resonant structure which occurs in the scattering cross section due to the formation of temporary negative-ion states. In common with elastic scattering at 0°, all of the partial waves by which the scattered electrons are represented are present at full strength. The forward elastic scattering, however, is not easily observed because of interference from the main unscattered electron beam. Of greater importance, from an experimental viewpoint, is the long path length for scattering which can be utilized in scattering at 180°. In studies of the differential scattering cross section, the effective path length for scattering is limited by the volume defined by the beam cone of the monochromator and the acceptance cone of the analyzer. At both 180° and 0°, the path length is maximized. A further advantage is evident for studies of compound-state formation in molecules in which the elastic scattering is strongly peaked in the forward direction because of electric dipole contributions to the cross section. The most sensitive technique currently in use for the detection of narrow resonances, electron transmission spectroscopy, detects a signal which is proportional to the total scattering cross section[1] or its derivative with respect to energy.[2] The portion of the total scattering which is due to resonances is therefore diminished when strong, nonresonant, forward scattering is present. Elastic scattering in the back direction is not influenced by the dipole contribution.

The measurement of low-energy electron scattering in the back direction is hampered by many experimental difficulties. Electron spectrometers which employ electric fields for energy selection suffer from the physical interference between the monochromator and the electron collector. Devices which use electron motion at right angles to a magnetic field[3] are able to separate the scattered electrons from the source. These spectrometers, however, are difficult to operate at low electron impact energies and, in many cases, possess inferior energy resolution.

We introduce here a new technique for the study of electrons which are elastically scattered from a gas target into a small solid angle centered at 180° with respect to the direction of the incident electron beam. The instrument is capable of energy resolution better than 40 meV full width at half-maximum and is useful over a wide range of impact energy. In this Letter, we have applied the technique to electron scattering from CO_2 vapor at energies from 3 to 5 eV. In this region the elastic cross section displays structure due to the presence of temporary negative-ion states.

The electron spectrometer is based on a simple modification to the trochoidal electron monochro-

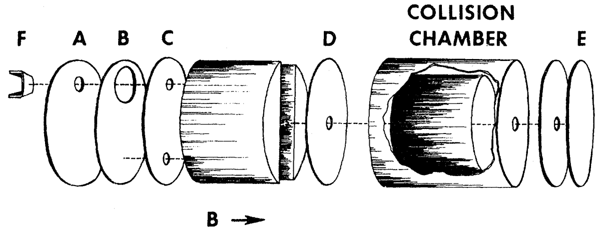

FIG. 1. Schematic diagram of the electron backscattering apparatus.

mator developed by Stamatovic and Schulz.[4] The energy resolution and ability to operate at low energy are features entirely attributable to the trochoidal monochromator. Figure 1 illustrates schematically the components of this apparatus. An electron beam, collimated by an axial magnetic field, is accelerated away from the filament through plate *A*. After passing through plate *B*, the beam is decelerated to low energy at plate *C* and passes into a region containing an electric field which is at right angles to both the incoming electron velocity and the magnetic field. The combined electric and magnetic fields cause the electrons to drift in a direction at right angles to both fields. The resultant displacement is a function of the time spent in the crossed field region. The electrons therefore disperse according to their axial velocity. A portion of the electrons pass through plate *D* and the energy-selected beam is accelerated into the collision chamber at any desired final energy. The energy resolution and operating characteristics of the trochoidal monochromator have been described in detail elsewhere.[4]

A characteristic of the motion in the crossed-field region is that the $\vec{E}\times\vec{B}$ drift experienced by the electrons takes place in the same direction regardless of the direction of motion along the axis of the tube. That is, electrons *entering* the crossed fields at plate *D* acquire a drift in the same direction as those entering at plate *C*. The electrons which are elastically scattered at 180° with respect to the incident beam in the collision chamber, therefore, can re-enter the crossed-field region at plate *D*. These electrons are again dispersed along the $\vec{E}\times\vec{B}$ direction. By opening a second hole in plate *C*, a portion of the elastically back-scattered electrons pass through and are collected at plate *B*.

To increase the dispersion in the trochoidal monochromator, the center potential in the crossed field region is normally adjusted so that the axial velocity of the electrons is very small. In the present application, this feature causes the monochromator to act as a discriminator against electrons which are scattered inelastically, or scattered elastically at angles outside of a small solid angle centered at 180°. These electrons do not have sufficient axial velocity to re-enter the crossed-field region.

To eliminate effects due to stray currents arriving at the collector plate *B*, the energy of the electrons in the collision chamber is modulated by means of a small ac voltage applied to a coaxial cylinder contained within the collision chamber. A lock-in amplifer is used to measure the scattered electron current arriving at the collector *B*. The signal therefore is proportional to the derivative of the differential elastic scattering cross section at 180°. In addition to the removal of stray currents, the measurement of the derivative has the effect of increasing the visibility of sharp structure appearing in the cross section. The same modulation technique has been recently used by Sanche and Schulz[2] to detect structure in the total scattering cross section of atoms and molecules.

In curve *a* of Fig. 2, the derivative with respect

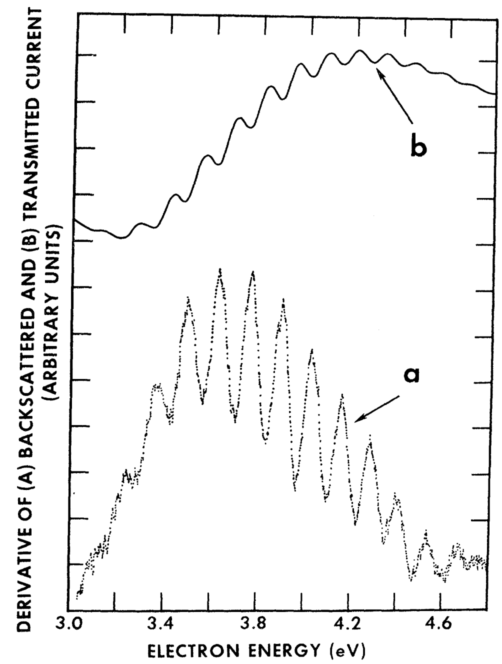

FIG. 2. Curve *a* shows the derivative with respect to energy of the electron current which is elastically scattered at 180° from CO_2 as a function of electron impact energy. Curve *b* shows the derivative of the transmitted current as measured by Sanche and Schulz. The vertical scales are not the same.

to energy of the electron current which is elastically scattered at 180° from CO_2 molecules is shown as a function of electron impact energy. The energy spread of the primary electron beam is 40 meV full width at half-maximum. The pressure of CO_2 in the collision chamber is 0.003 Torr. The length of the collision chamber is 2.5 cm. The data shown in Fig. 2, curve *a*, were taken with a single scan through the energy range with a time constant of 30 sec.

The elastic scattering cross section from 3.0 to 4.8 eV exhibtis considerable structure due to the presence of short-lived states of CO_2^-. The series of peaks shown here has an average spacing of 130 ± 3 meV. This structure was first observed in the total scattering cross section in an electron transmission experiment by Boness and Hasted.[5] Because of instrumental background effects, the peaks had rather low visibility and the spacing appeared somewhat irregular. The average spacing was 127 meV. Structure spaced at 131 ± 5 meV was found by Andrick and Danner[6] both in the differential elastic cross section and in the excitation functions of the symmetric stretch and bending modes of the electronic ground state.

A recent transmission experiment showing the structure as it appears in the total scattering cross section was carried out by Sanche and Schulz.[7] In this experiment the derivative with respect to energy was measured directly and hence a comparison with the present data is very conveniently made. The transmission data of Sanche and Schulz are shown in curve *b* of Fig. 2. Because their signal is proportional to the derivative of the unscattered current, the peaks in curve *b* correspond to the dips in curve *a*.

Interference between resonant and potential scattering causes the differential elastic scattering cross section to change shape as a function of scattering angle. The total scattering cross section and the differential elastic cross section at 180° are therefore not expected to have the same energy dependence in the region of the resonances. In CO_2, the cross section for backscattering exhibits the peaked structure as a greater fraction of the total signal excursion than does the total scattering cross section. This allows a more accurate study of the structure than was available previously.

Claydon, Segal, and Taylor[8] have calculated several of the potential curves of the CO_2^- system as a function of the symmetric stretching vibrational coordinate and of the bending angle. They find that the $CO_2^-(^2\Pi_u)$ state occurs at the proper energy to explain the resonant behavior in the cross section. Furthermore, they find that the equilibrium bond length of the $CO_2^-(^2\Pi_u)$ state is longer than that of the CO_2 ground state. This implies that the negative ion begins to move in the symmetric stretch mode immediately after the time of formation of the compound state. If the period of vibration is comparable to or shorter than the lifetime of the negative ion, the scattering cross section will exhibit vibrational structure. The diatomic analog of this phenomenon is well established.[9] The series of peaks seen in Fig. 2 can therefore be ascribed to be the symmetric stretch vibration of the $CO_2^-(^2\Pi_u)$ state.

Claydon, Segal, and Taylor[8] have calculated the equilibrium bond angle for the ground state of CO_2^- to be 137°. Because bending as well as symmetric stretching of the molecular ion is initiated as soon as the compound state is formed, one expects that structure in the elastic scattering cross section due to bending would also appear. Despite the good visibility of the symmetric stretch structure as seen in Fig. 2, no evidence for other vibrational modes is seen. A rather simplified model with respect to the lifetime of the compound state can be made in order to understand the absence of the bending mode. Although the autoionization lifetime in CO_2^- is a function of all the nuclear coordinates, we assume that there is only a single average lifetime associated primarily with motion along the symmetric stretch coordinate. Because CO_2^- is linear when it is formed, the bending mode is highly excited. Furthermore, the calculation of Claydon, Segal, and Taylor also shows that the variation of potential energy with bending angle near 180° is rather small. These considerations suggest that the period of oscillation for the highly excited bending mode will be long compared with that of the symmetric stretch. The compound state therefore may not last long enough to allow a large excursion in bending angle and the subsequent reflection of the nuclear wave function necessary to produce bending mode structure.[9]

An estimate of the autoionization width of the compound state may be made from the data in Fig. 2 and knowledge of the electron energy distribution. From the extent of peak overlapping, the average autoionization width lies between 0.13 and 0.26 eV.[10]

As discussed previously by Boness and Schulz,[11] a separate estimate of the autoionization width may be made by use of the measured cross section for production of O^- which takes place through the compound state. The dissociative attachment cross section is given[12] by $Q_- = Q_0 \exp(-\bar{\Gamma}\tau/\hbar)$, where Q_- is the cross section for production of O^-, Q_0 is the cross section for formation of the compound state, $\hbar/\bar{\Gamma}$ is the average lifetime of the compound state, and τ is the stabilization time. Using the period of oscillation in the compound-state symmetric stretch mode as a typical stabilization time, we have $\tau \simeq 3\times 10^{-14}$ sec. With the values[13,14] $Q_- = 1.5\times 10^{-19}$ cm^2 and $Q_0 = 4\times 10^{-15}$ cm^2, we obtain $\bar{\Gamma} \simeq 0.2$ eV, which is in good agreement with the value deduced from Fig. 2. This agreement also supports the simple model using only a single average lifetime for the compound state.

The influence of the compound state on the cross sections for excitation of the vibrational modes of the ground electronic state has been studied by Boness and Schulz[11] and Andrick and Danner.[6] Strong excitation of both the symmetric stretch and bending modes was found. The cross section for excitation of the asymmetric stretch mode was at least an order of magnitude less than that for the other two modes.[6]

The angular dependence of inelastically scattered electrons measured by Andrick and Danner[6] has been analyzed recently by Andrick and Read.[15] Using symmetry arguments they conclude that the angular distributions support the hypothesis that the compound state is nearly linear. The lifetime inferred here together with the absence of structure due to the compound-state bending mode also support this hypothesis.

We point out, in conclusion, that the technique introduced here for the study of elastic scattering at 180° is not restricted in principle to collisions in gases and should also find application in studies of electron scattering from surfaces.

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[10] If the autoionization width exceeds twice the vibrational spacing, the apparent half-width of the peaks becomes equal to half the vibrational spacing. This is borne out by backscattering data in N_2 in which this condition holds according to Ref. 9. In CO_2, however, the measured half-width of the peaks is less than half the vibrational spacing. This gives an upper limit on the autoionization width of 0.26 eV.

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[14] For Q_0 we have used the theoretical maximum value for p-wave scattering. As pointed out in Ref. 11, this overestimates the true value. The calculation is not sensitive to this parameter.

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